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14. ABSTRACT Among thermosetting resins, polycyanurate networks (derived from cyanate ester monomers) offer excellent flame, smoke, and toxicity characteristics along with enhanced thermo-oxidative stability compared to epoxy resins. Recent structure-property investigations in polycyanurate networks have revealed new insights into the relationship between the chemical moieties found in the networks and the corresponding levels of thermo-oxidative resistance. In particular, it appears that the presence of methyl groups next to tertiary or quaternary carbons has a decidedly negative impact on thermo-oxidative stability during TGA heating ramp tests. In the case of silicon-containing cyanate esters, thermo-oxidative stability can be improved significantly by the incorporation of silicon only in cases where either a large portion of the chemical repeat unit is formed from inorganic groups, or the thermo-oxidative stability of the carbon-containing analog is relatively poor compared to other organic polycyanurate networks.					
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NEW APPROACHES TO MAXIMIZING THERMO- OXIDATION RESISTANCE OF POLYCYANURATE NETWORKS

13 August 2014

**Andrew J. Guenthner¹, Matthew C. Davis², Vandana Vij³,
Gregory R. Yandek¹, Kevin R. Lamison³, Josiah T. Reams³,
Timothy S. Haddad³, Joseph M. Mabry¹**

¹Aerospace Systems Directorate, Air Force Research Laboratory

²Naval Air Warfare Center, Weapons Division

³ERC Incorporated

Ph: 661/275-5769; e-mail: andrew.guenthner@us.af.mil

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Outline



- Role of Bridge Type:
 - Avoid Ethylidene and Isopropylidene Bridges!
- Role of Si
 - High Inorganic Content Needed to Match the Gains from Proper Selection of Bridge Type
- Bio-based Materials
 - Resveratrol-based CE Delivers Exceptional Thermal Stability and Fire Resistance



Acknowledgements: Strategic Environmental Research and Development Program (SERDP); Air Force Office of Scientific Research (AFOSR) – program support; PWG Team Members!





Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

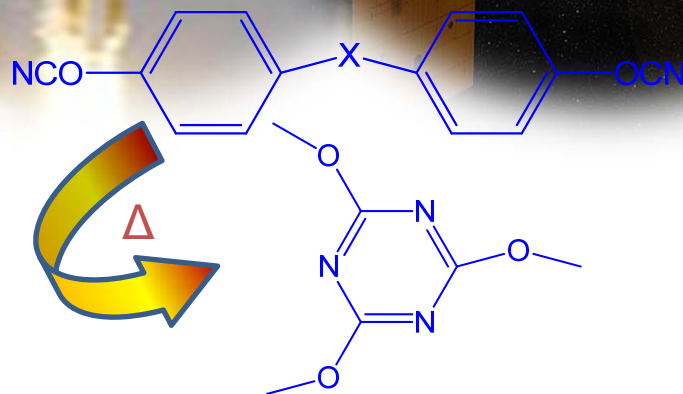
Onset of Weight
Loss:
> 400 °C with High
Char Yield

Ease of
Processing

Resistance to
Harsh
Environments

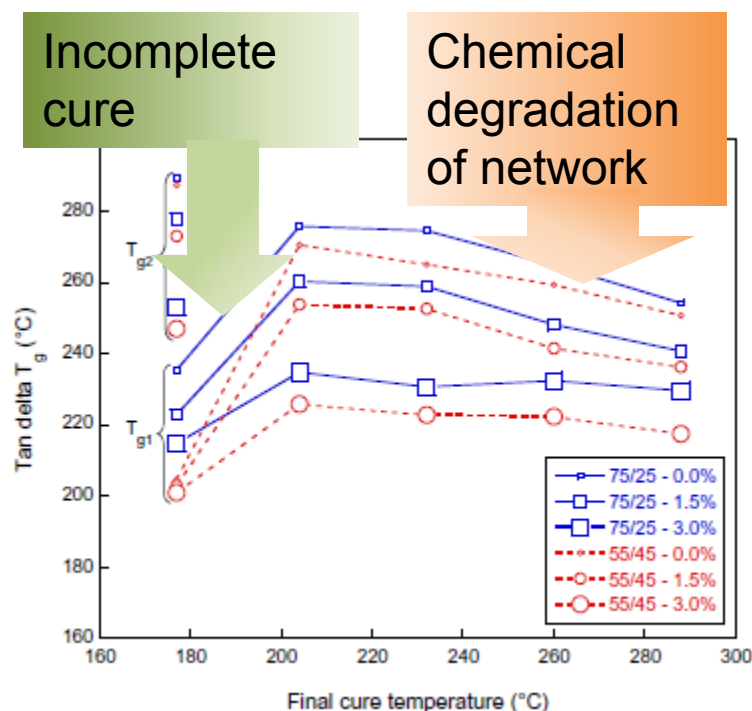
Good Flame,
Smoke, &
Toxicity
Characteristics

Low Water Uptake
with Near Zero
Coefficient of
Hygroscopic
Expansion





Thermo-mechanical versus Thermo-chemical Stability



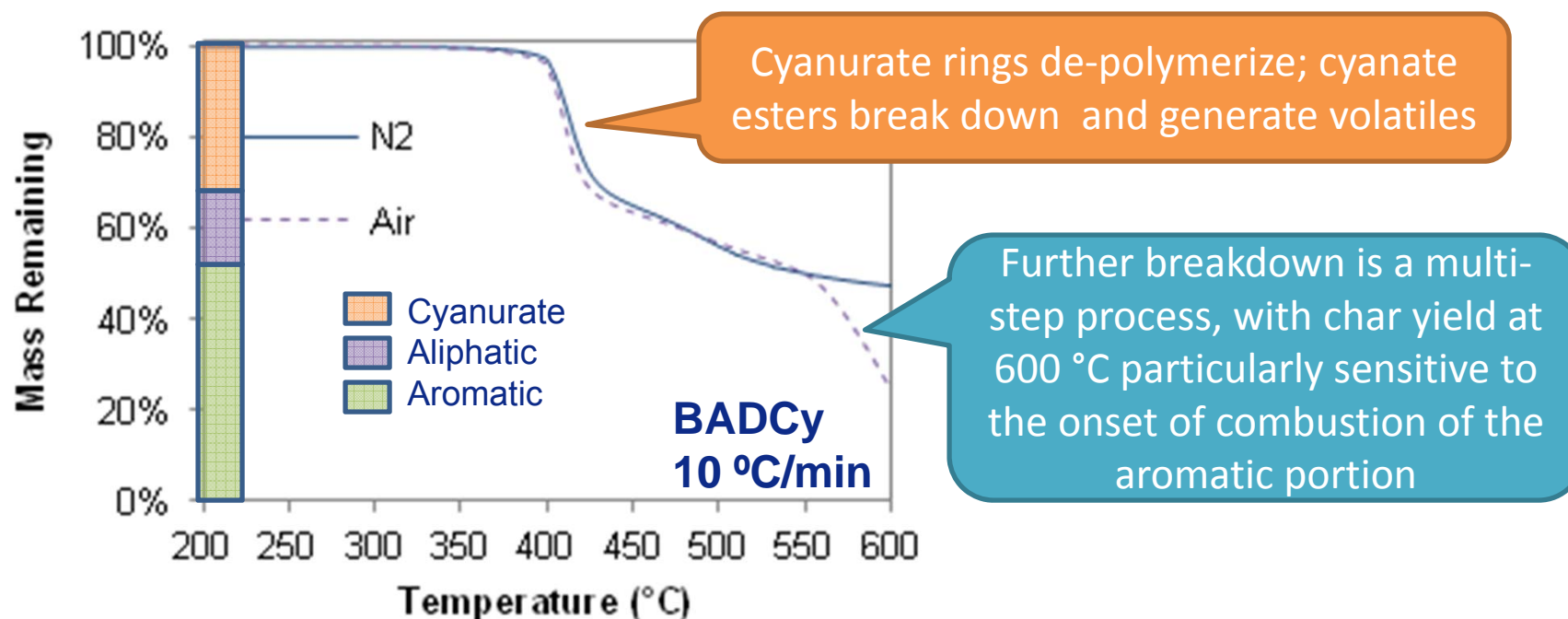
Goertzen, W. K.; Kessler, M. R. *Composites: Part A* **2007** 38, 779–7, Fig. 6, for blends of EX1551 / EX1510 – catalyst.

- The more rigid the network, the higher the thermo-mechanical stability (i.e. softening point for a given network structure).
- Many networks cannot achieve their maximum possible thermo-mechanical stability because at the high temperatures needed for cure, chemical bonds break (i.e. thermochemical stability is limited).
- Typically, adding flexible chemical linkages (such as aliphatic groups) to the chemical structure of a monomer will reduce the rigidity, facilitating the achievement of full cure, but at the expense of thermo-chemical stability.

Needed: a flexible chemical linkage that enables full cure of cyanate esters at acceptable temperature-catalyst combinations while maintaining the desirable chemical degradation characteristics (both rates and char yields) of rigid systems



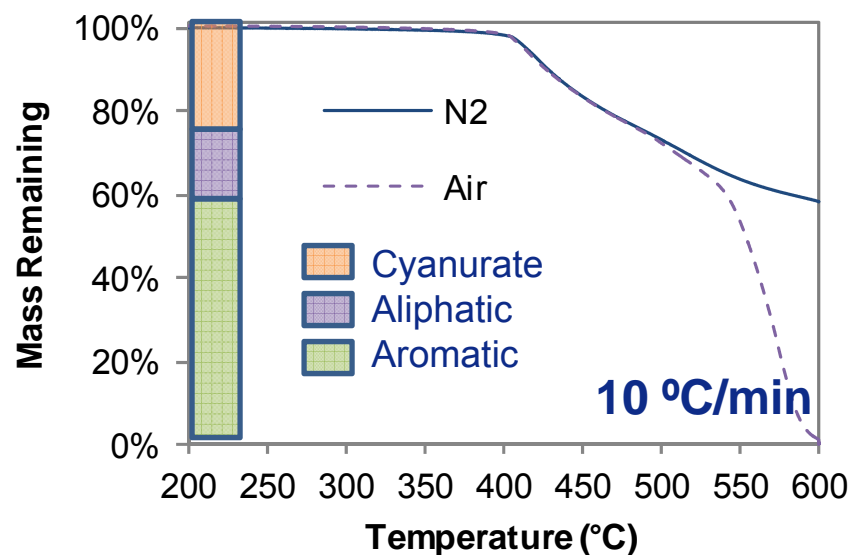
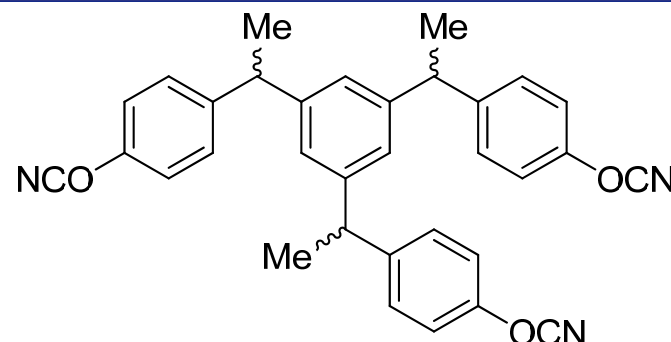
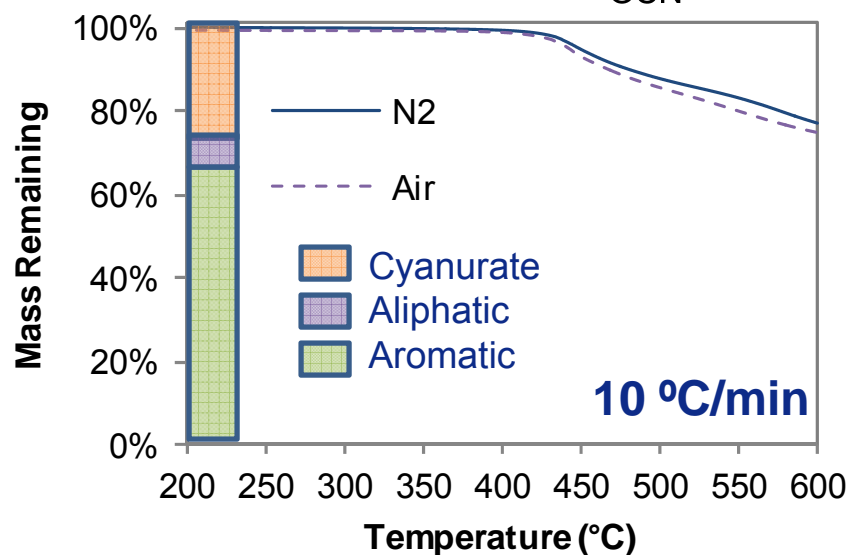
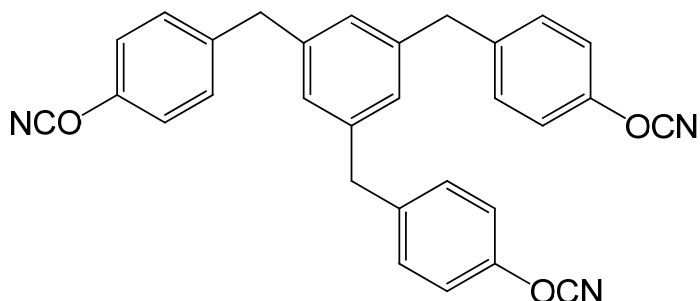
TGA of Cyanate Esters



- TGA provides a simple tool to assess onset temperatures, rates, and char yields associated with the decomposition of cyanate ester networks.
- A reasonably slow TGA scan also drives all cyanate ester systems close to the maximum possible extent of conversion (via *in-situ* cure) at the point where decomposition begins.



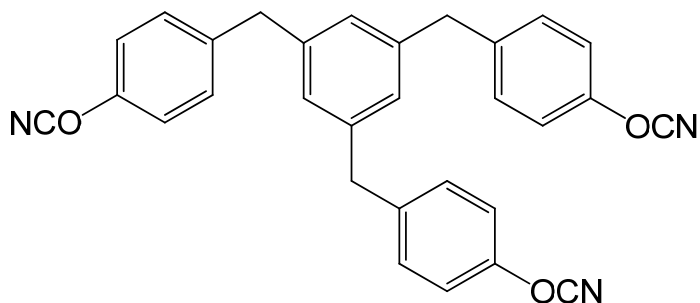
Cyanate Ester TGA: Methylene versus Ethylidene Segments



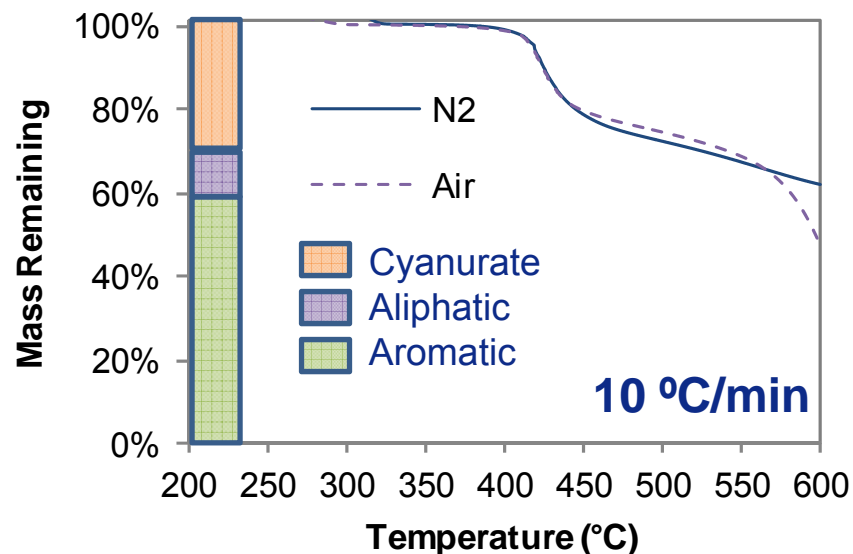
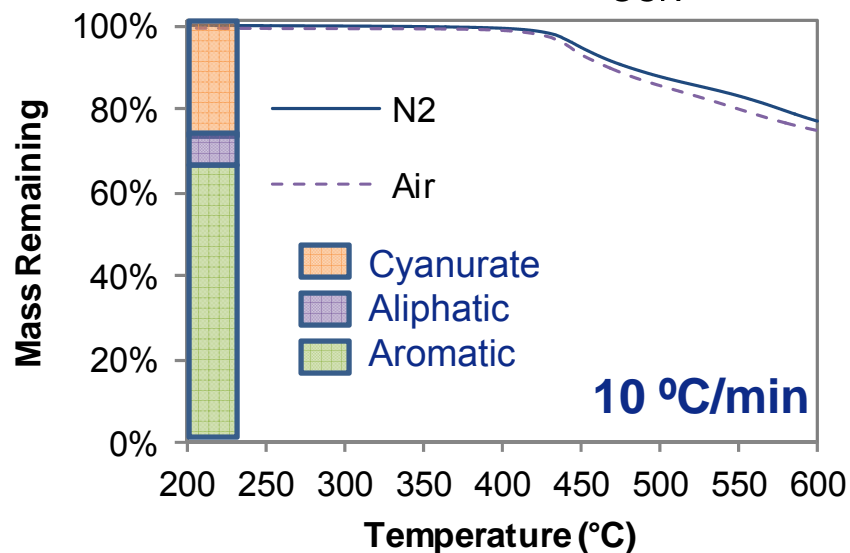
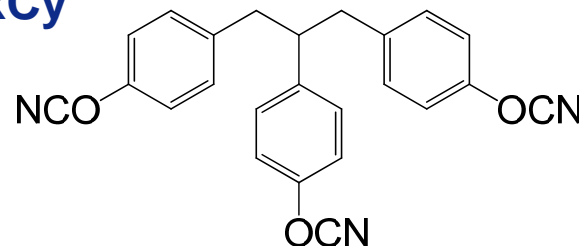
- The tricyanate with methylene segments shows delayed onset of degradation, reduced decomposition rates, and very high char yield.
- The tricyanate with ethylidene segments behaves much like BADCy when taking into account the composition, with slightly earlier aromatic combustion.



Cyanate Ester TGA: Aliphatic *versus* Aromatic Junctions



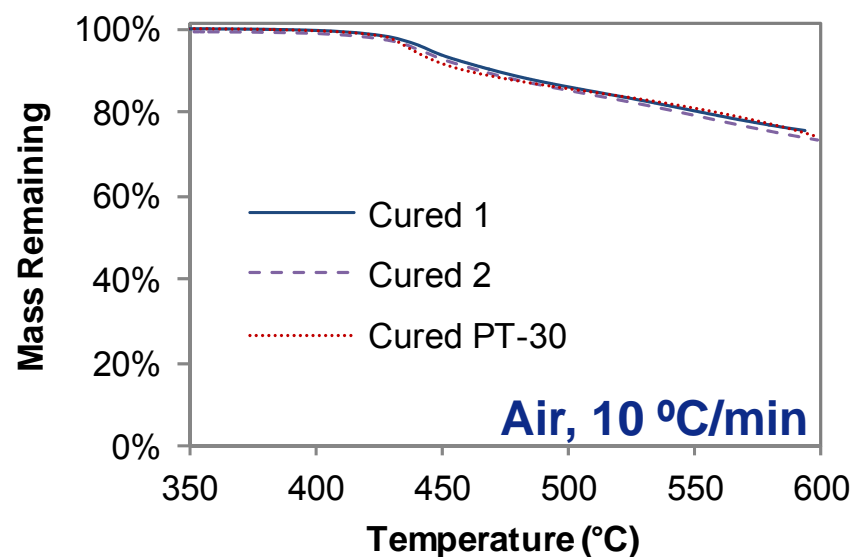
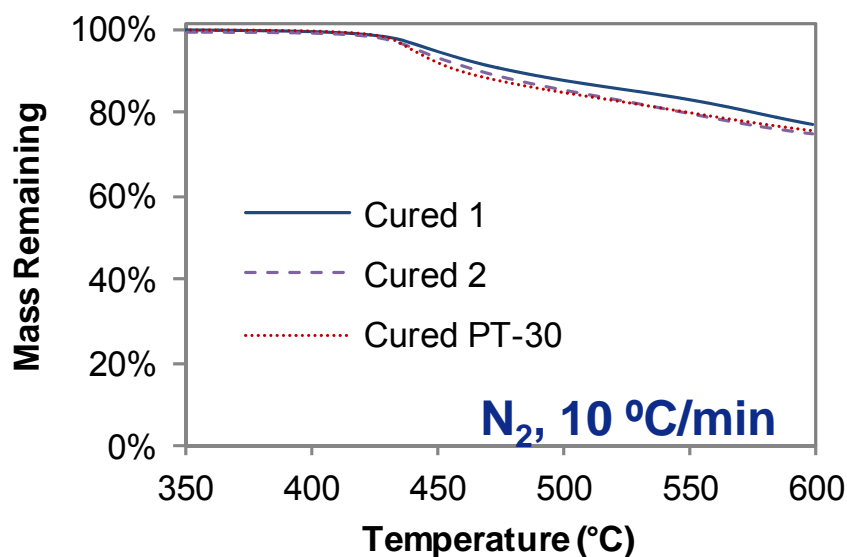
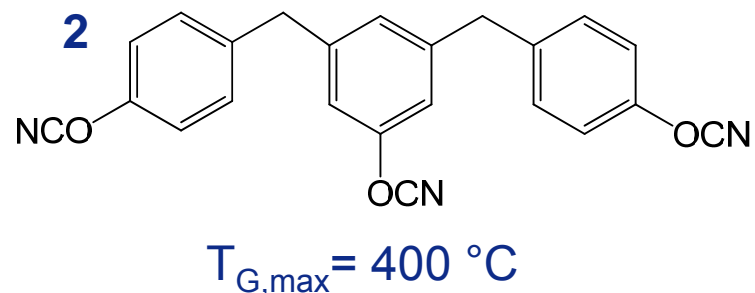
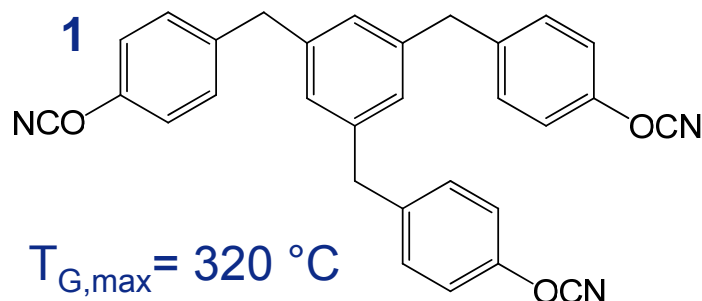
“FlexCy”



- The tricyanate with the aliphatic junction (tertiary carbon) also follows the pattern for BADCy, taking into account composition, with a slightly delayed onset of aromatic combustion compared to BADCy.



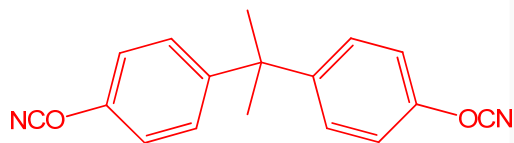
Segment Flexibility Can Be Tuned Without Affecting Char Yields



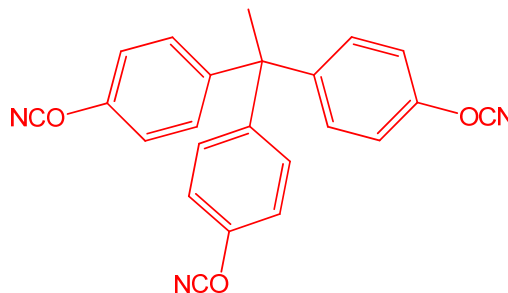
- Note that PT-30 is similar to an oligomeric version of **2**.
- Tuneability of $T_{G,max}$ enables full cure to be achieved with a wider range of catalysts under typical processing constraints.



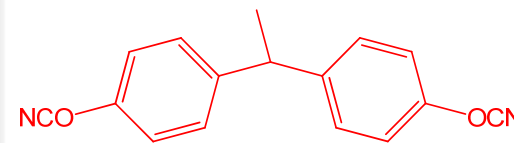
Si-Containing Cyanate Ester Monomers



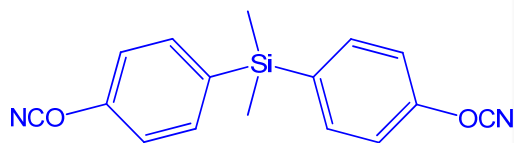
BADCy



ESR255



LECy



SiMCy



STT3

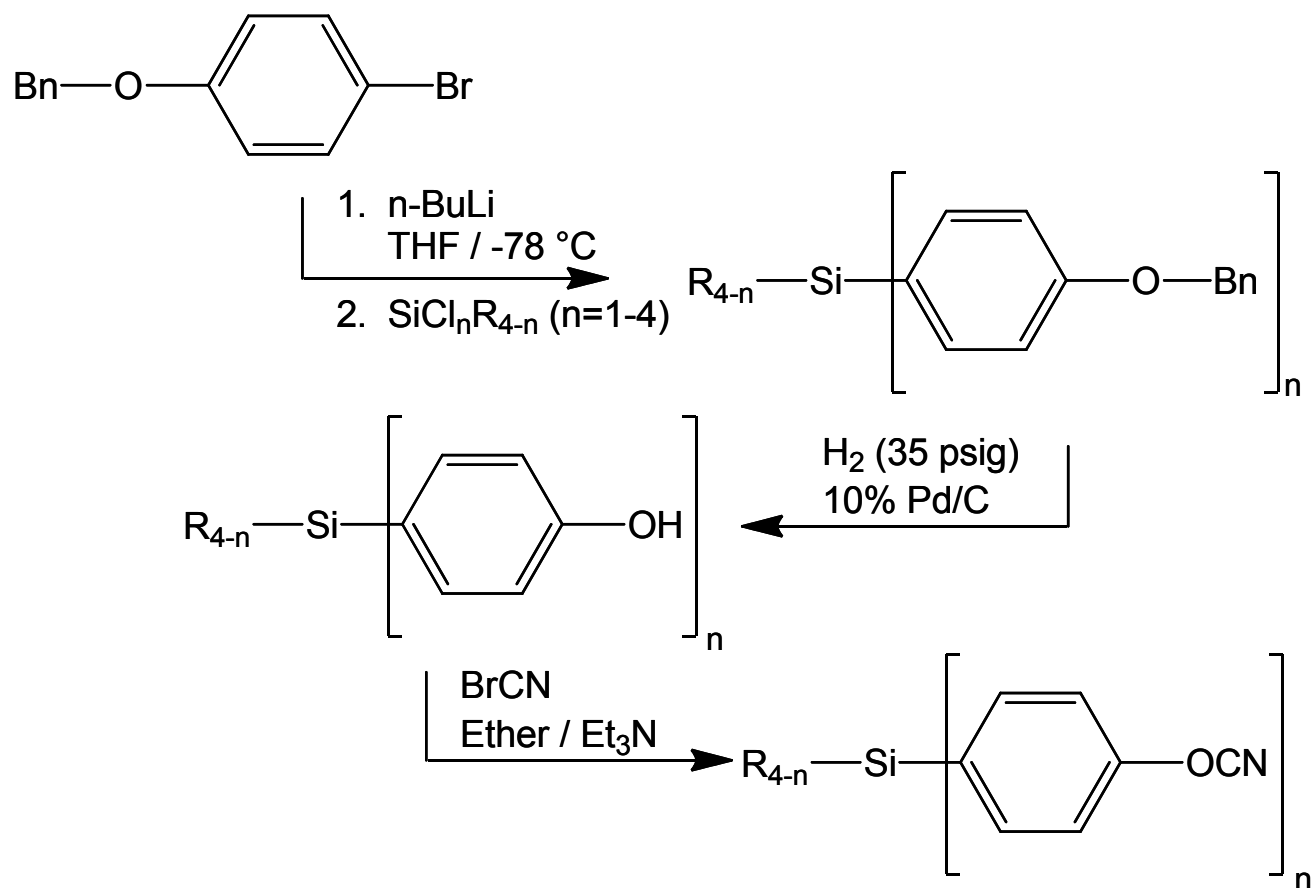
Catalyzed systems use:

160 ppm Cu(II) as Cu(II)(acac)_2
with 2 phr nonylphenol

All samples were melted, blended, and de-gassed for 30 min. prior to cure in silicone molds under N_2 , cure schedule for 1 hr at 150 °C followed by 24 hrs at 210 °C, with ramp rates at 5 °C / min.



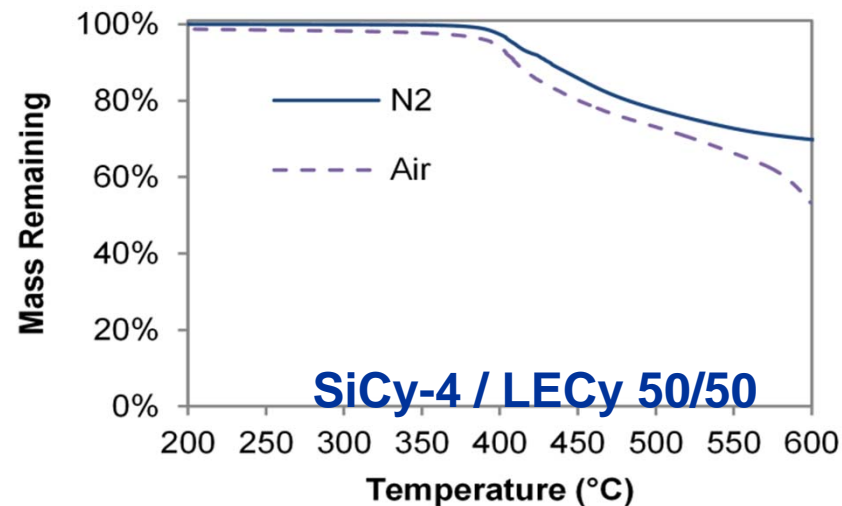
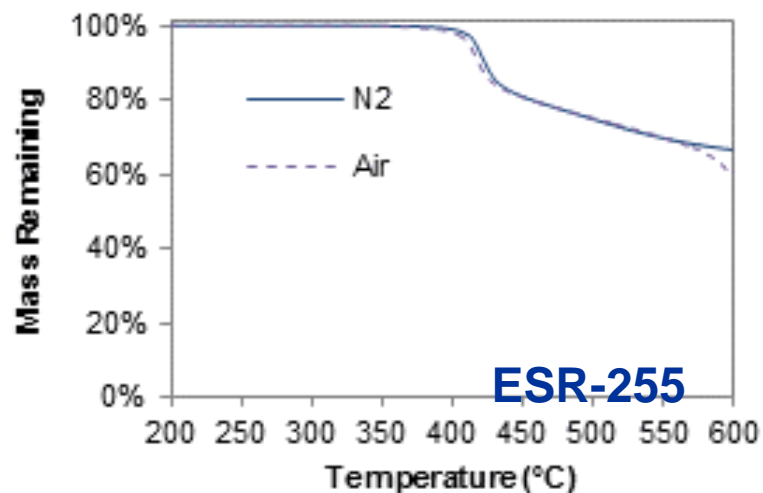
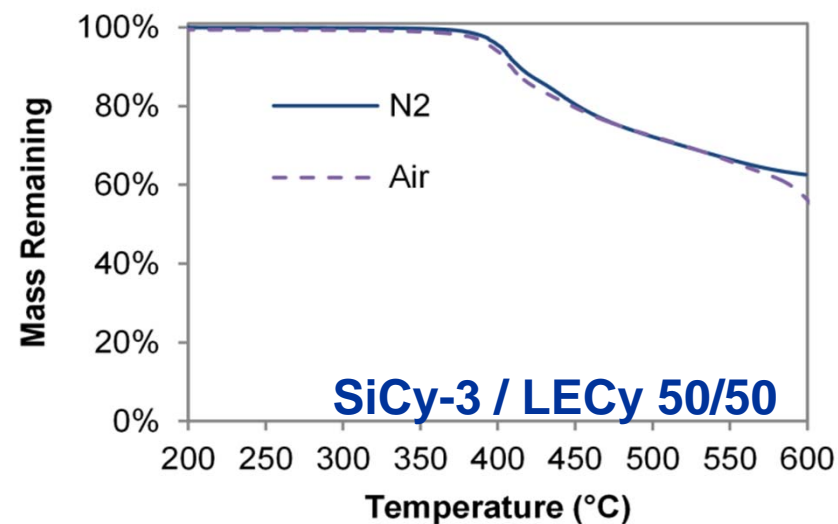
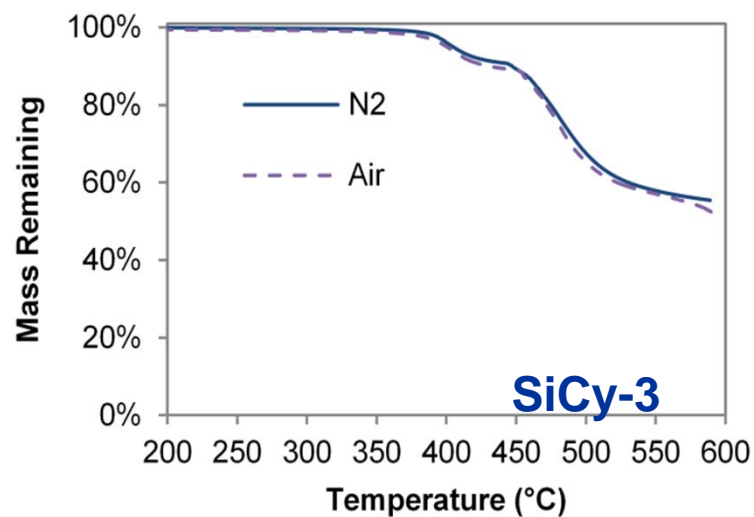
General Synthesis for Si-Containing Monomers



- SiMCy is the $n=2$ case (Si in network segment), $n=3$ or $n=4$ produces Si at network junctions.



Si-Containing Cyanate Esters: TGA Data





Si-Containing Cyanate Esters: Non-isothermal DSC



Comparative TGA Data for Cyanate Ester Monomers Cured at 210 °C for 24 hours

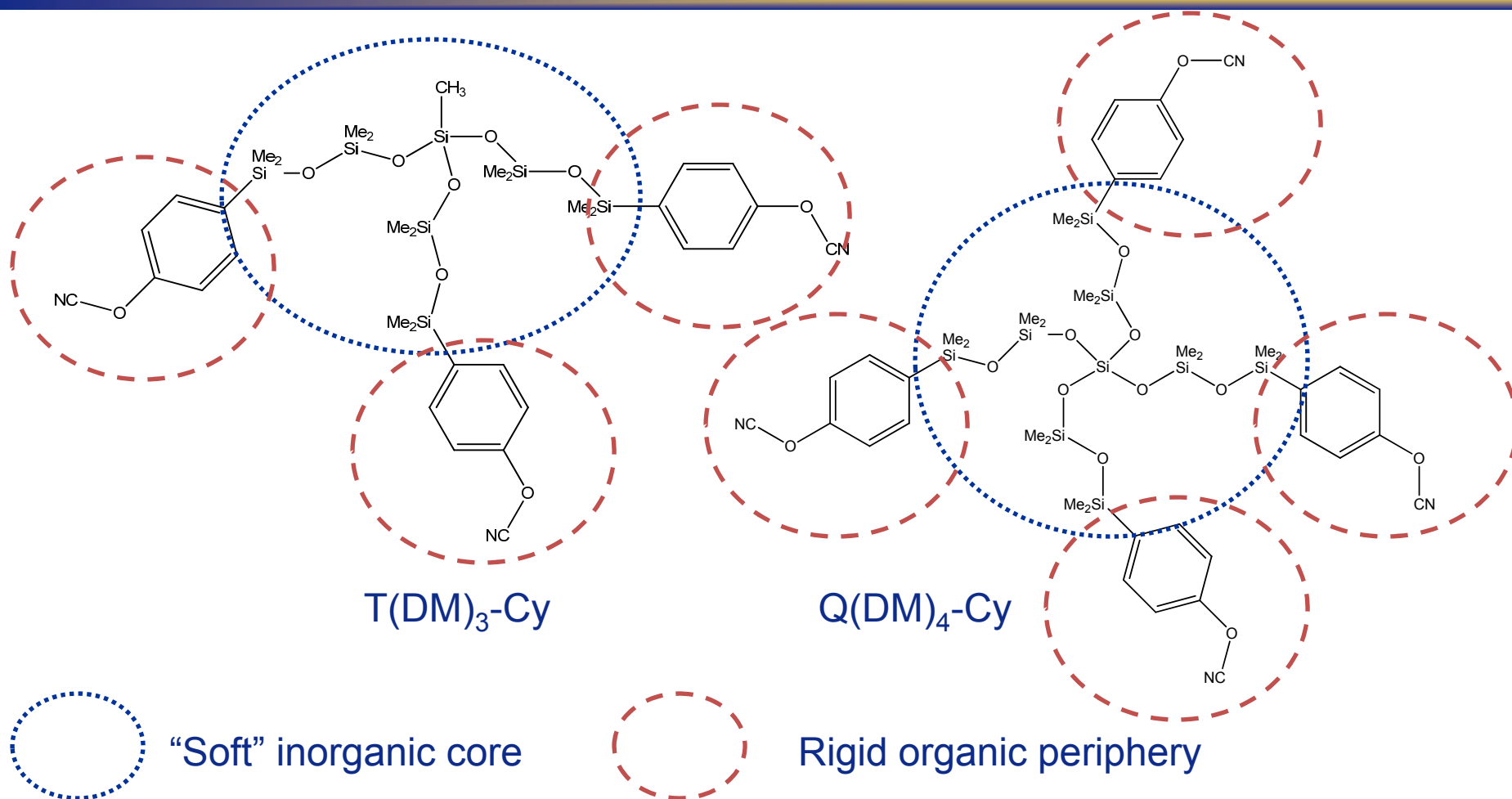
Monomer	Central Atom	<i>f</i>	Purification	T, 5% wt. Loss (in N ₂ , °C)	T, 5% wt. Loss (in air, °C)	Char Yield (in N ₂ , 600 °C)	Char Yield (in air, 600 °C)
BADCy	C	2	As-Rec'd	402	400	47%	25%
ESR-255	C	3	As-Rec'd	417	412	67%	59%
SiMCy	Si	2	As-Synth.	422 ^a	409 ^a	43%	50%
SiCy-3	Si	3	As-Synth.	405	400	55%	50%
SiCy-3 / LECy	Si	3 / 2	As-Synth.	402	396	63%	56%
SiCy-4 / LECy	Si	4 / 2	As-Synth.	409	395	70%	53%
ESR-255 / LECy	C	3 / 2	As-Rec'd	405	406	60%	2%

^a Estimated

- Substitution of Si for C at the bridge only improves char yields when those yields are low. For organic cyanate esters with high char yields, substitution of Si is not helpful.
- Incorporating monomers with greater functionality is most effective at raising char yields in nitrogen.



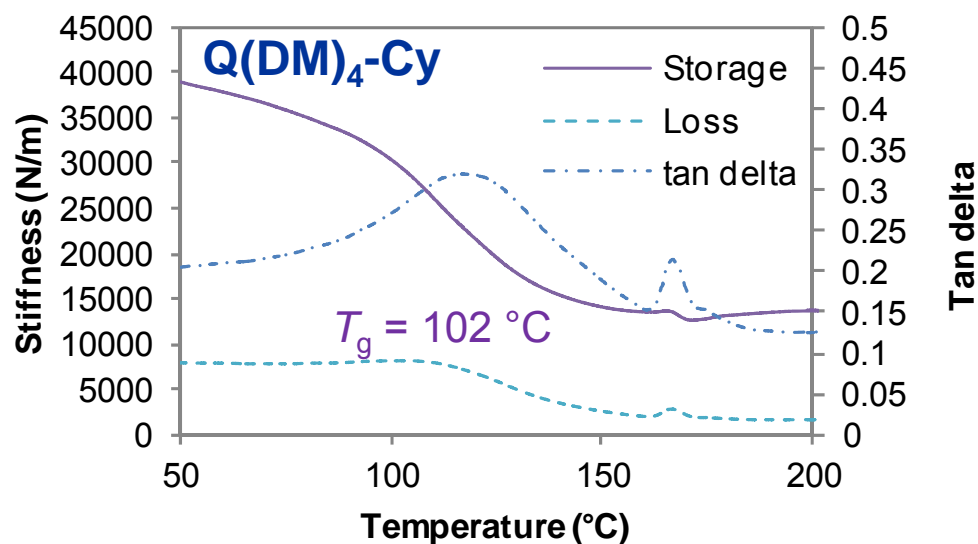
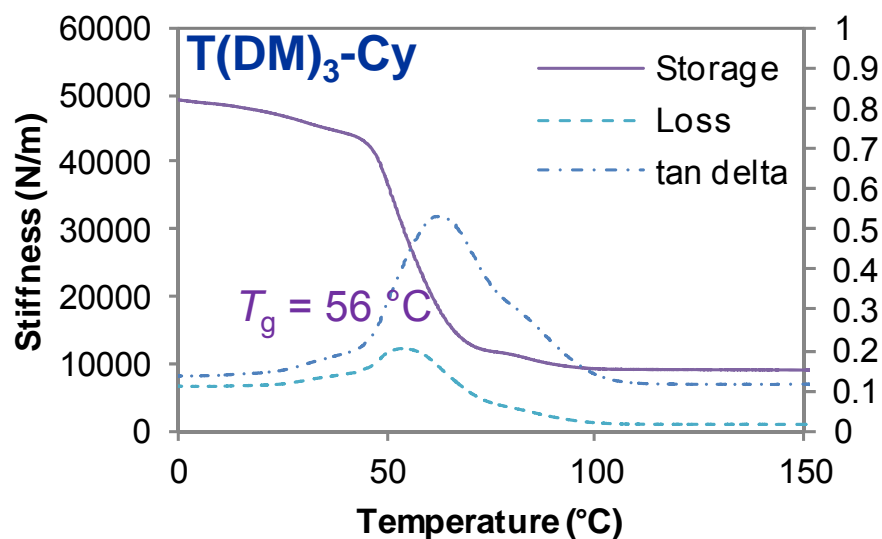
Siloxane-Containing Cyanate Esters



- Higher inorganic content expected to result in better char yields at temperatures over 600 °C.



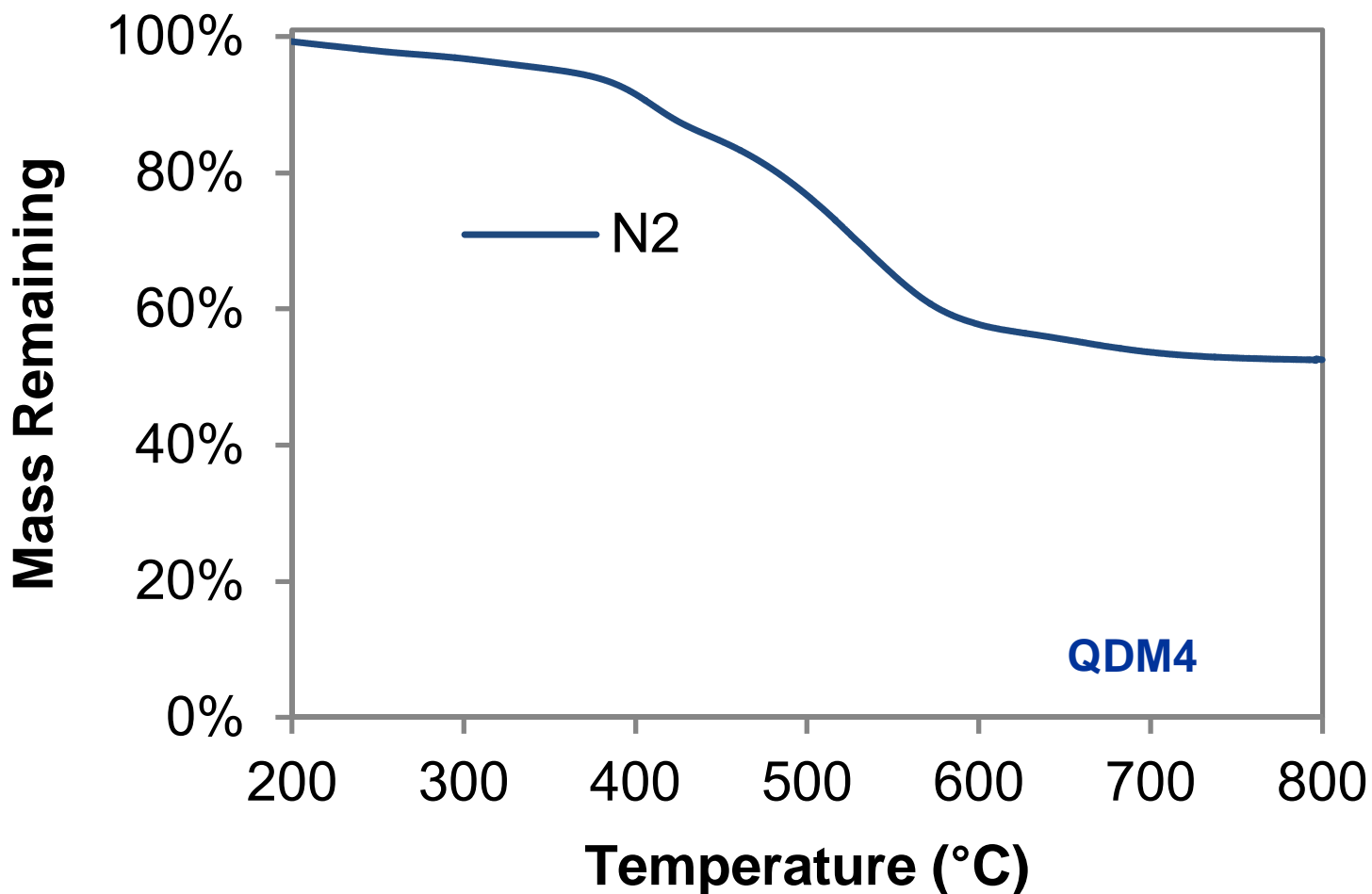
Siloxy-Containing Cyanate Esters: Glass Transition Temperature



- Both cyanate esters showed a relatively low glass transition temperature for cyanate esters.
- The cyanurate density for these resins is roughly half that of typical cyanate esters.
- The branch point adds some stiffness, but not enough to make up for the long distance between network junctions.
- Further optimization of the cross-link and junction density will be needed to produce cyanate esters with both flexible core regions and high glass transition temperatures.



Siloxane Cyanate Esters: Preliminary TGA Data

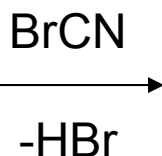
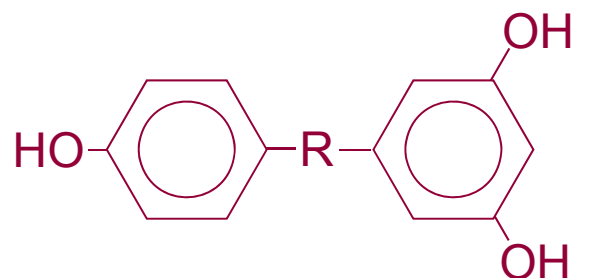




Fire-Resistant Cyanate Esters From Resveratrol

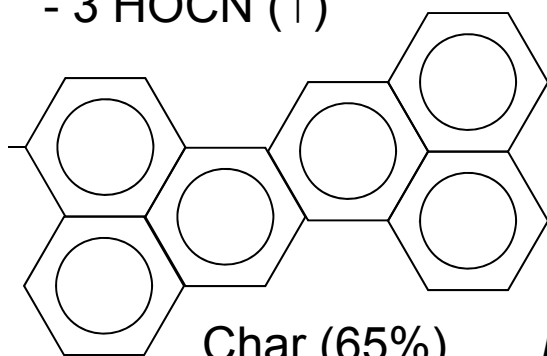


- Polyphenolic antioxidant used as a dietary supplement
 - Extracted from seaweed, red grapes, red wine



$R = -\text{HC}=\text{CH}-$, $= -\text{CH}_2-\text{CH}_2-$
(resveratrol) (dihydro resveratrol)

- 3 HOCN (\uparrow)

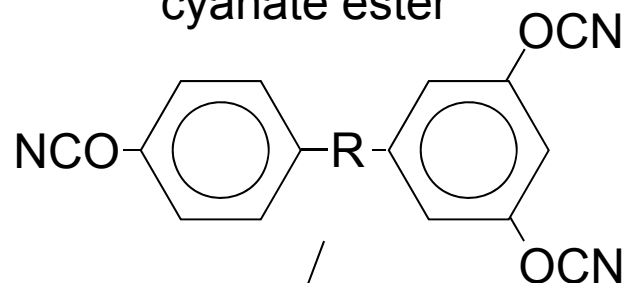


Char (65%)

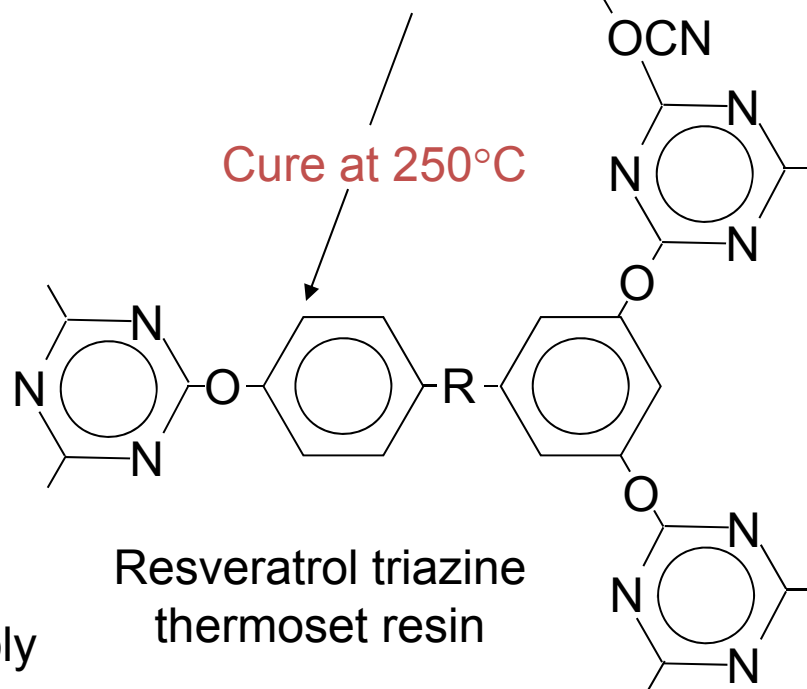
$H_c \approx 3 \text{ kJ/g-poly}$

Fire
> 450°C

Resveratrol
cyanate ester*



Cure at 250°C

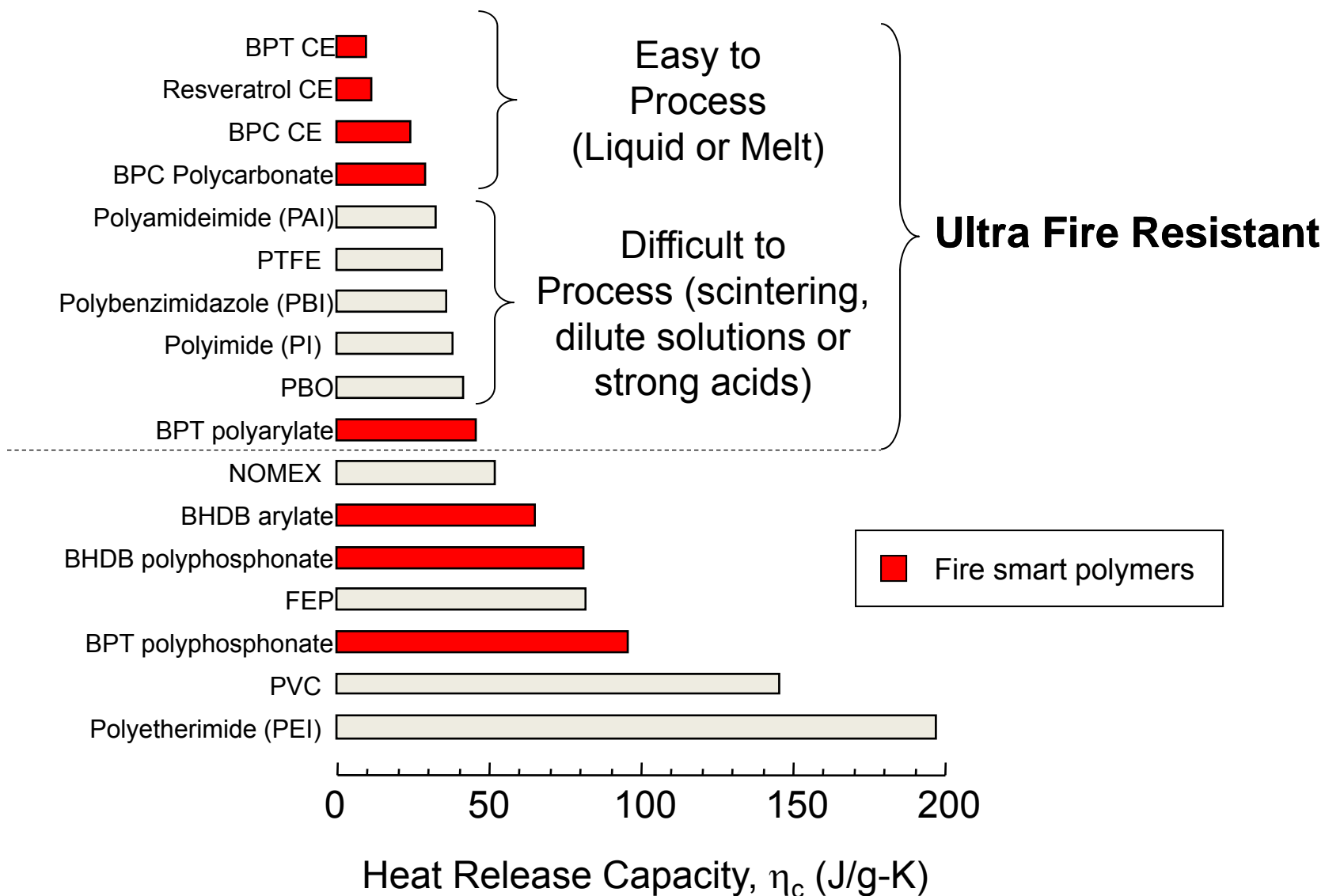


Resveratrol triazine
thermoset resin

*B.J. Harvey, et. al., SERDP WP-2214 SEED Final Report, U.S. Navy, NAWCWD, China Lake, CA (2011), as presented by R. Lyons at *Meeting High Performance Flammability Requirements for Aviation*, Seattle, WA, April 2-3, 2014



Fire Smart Versus Current 65/65 Polymers



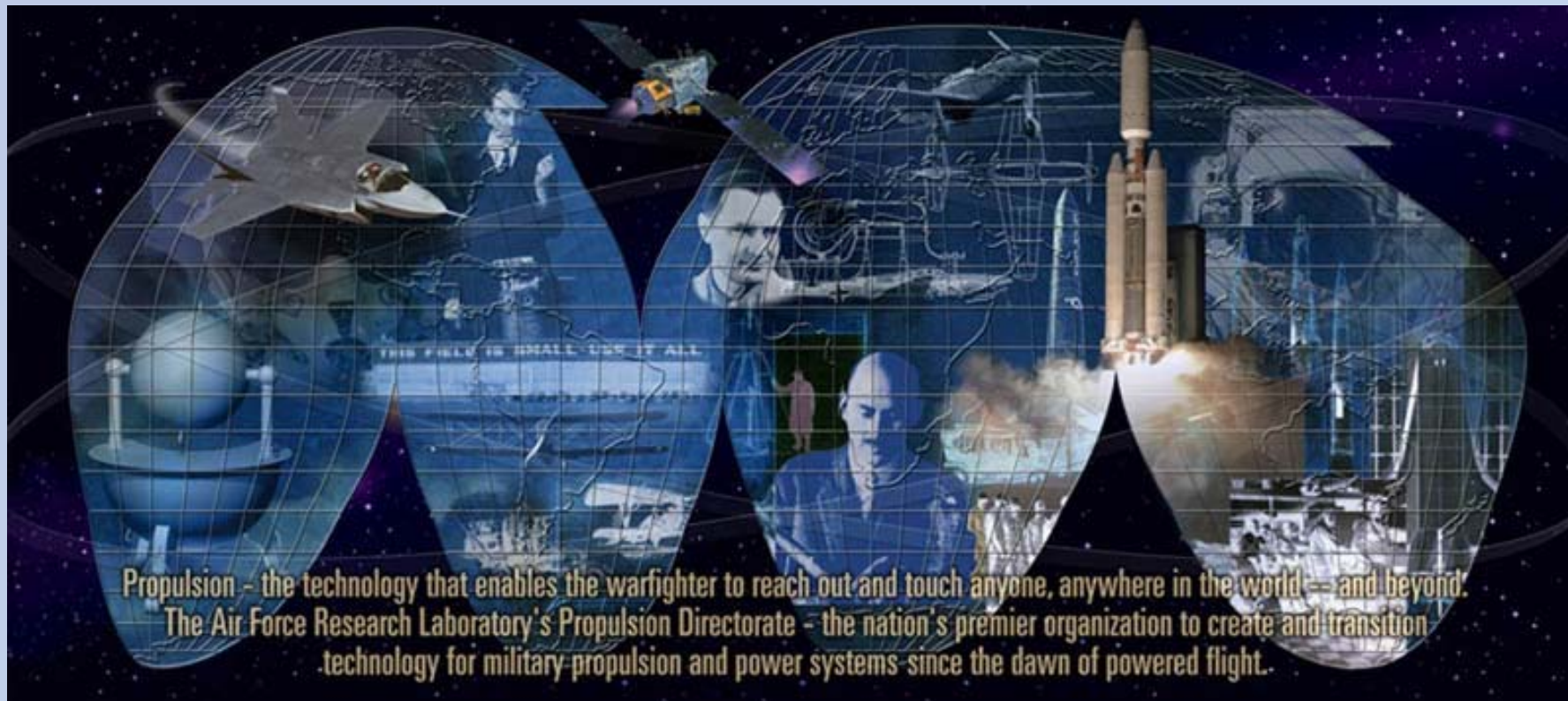
As presented by R. Lyons at Meeting High Performance Flammability Requirements for Aviation, Seattle, WA, April 2-3, 2014

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Summary

- The short-term chemical stability of cyanurate networks appears to be optimal when segments and junctions containing tertiary or quaternary carbons are avoided (based on empirical observation but supported by studies in polycarbonate).
- Using combinations of methylene and phenylene junctions and spacers in cyanurate networks, the T_G -conversion characteristics can be tuned to match processing constraints without sacrificing thermochemical stability.
- Incorporation of inorganic Si or siloxane moieties in cyanate esters is only helpful for thermo-chemical stability at very high temperatures and when a large portion of the monomer consists of inorganic moieties.
- Cyanate esters based on resveratrol show good short-term thermo-oxidation resistance as well as very promising fire resistance characteristics based on preliminary investigations to date.



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